

THE POSSIBILITIES OF OBTAINING LONG-RANGE SUPPLIES OF URANIUM, THORIUM, AND OTHER SUBSTANCES FROM IGNEOUS ROCKS

By HARRISON BROWN and LEON T. SILVER, California Institute of Technology

CONTENTS

	Page		Page
Abstract.....	91	Processing.....	94
Introduction and acknowledgments.....	91	Energetics and cost.....	94
Distribution of uranium and thorium in igneous rocks.....	92	Conclusions.....	95

ILLUSTRATION

	Page
FIGURE 12. Rate of solution of radioactive materials from several granites.....	93

TABLES

	Page		Page
TABLE 1. Distribution of uranium and thorium in granite from Essonville, Ontario.....	92	TABLE 3. Composition of leaches from several pulverized granites.....	93
2. Gross chemical composition of leaches from several types of rocks.....	93	4. Distribution of alpha tracks in thin-section autoradiographs of several granitic rocks.....	93

ABSTRACT

Most uranium and thorium which have been produced in the world thus far have been obtained from ores of relatively high grade. Such deposits are not very extensive and are found infrequently. When the high-grade deposits of these substances approach exhaustion, it may be that material containing these elements in low concentrations will be the ultimate source.

An average granite contains about 4 ppm uranium and 12 ppm thorium. If all the uranium and thorium in 1 ton of average granite could be extracted and utilized by means of nuclear breeding, the energy output would be equivalent to that obtained by burning 50 tons of coal. Means are now available for relatively easy extraction of about one quarter of the uranium and thorium from average granite, with an energy profit per ton of rock processed equivalent to that obtained by burning 10 tons of coal.

Results also indicate that a variety of both major and minor substances of industrial importance can be obtained as byproducts of uranium and thorium production from igneous rocks.

The techniques required for extracting uranium and thorium from igneous rocks are well within the realm of present mineral-dressing and industrial-chemical experience.

INTRODUCTION AND ACKNOWLEDGMENTS

As the world demand for uranium and thorium increases, the materials which contain these elements in low concentration will have to be used. If atomic energy were to supply a substantial fraction of the world's

power requirements, the drain on high-grade deposits would be particularly rapid, primarily as the result of the huge inventories required for reactor construction. For example, power-breeder reactors may necessitate uranium inventories which are more than 500 times the yearly consumption of uranium by neutron capture and fission.

Looking into the future, it is important to know whether a nation devoid of high-grade deposits can obtain uranium from substances which exist in abundance on the earth's surface.

In an attempt to answer this question, this investigation of the possibilities of isolating uranium and thorium from igneous rocks was undertaken. Igneous rocks were chosen for study because they exist in abundance on the earth's surface, and preliminary information indicated that uranium and thorium are localized in crystalline rocks in such a way as to facilitate extraction by chemical and physical means.

The authors of this report wish to acknowledge the work on this investigation by their colleagues W. J. Blake, A. A. Chodos, Richard Kowalkowski, C. R. McKinney, and Aiji Uchiyama of the California Institute of Technology, and G. J. Neuberger of the U. S. Geological Survey.

DISTRIBUTION OF URANIUM AND THORIUM IN IGNEOUS ROCKS

Igneous rocks consist of assemblages of minerals which possess diverse compositions and structures. During the process of rock formation, those elements which exist in such low abundance that they are unable to form separate minerals distribute themselves among the major minerals in proportions determined by the structures of the minerals and by the chemical properties of the elements. Both uranium and thorium possess ionic radii and charges which prevent them from fitting comfortably into the lattices of any of the common major minerals of granite, but they fit into certain of the accessory minerals, such as zircon, allanite, sphene, and apatite. In zircon, for example, uranium and thorium in the (+4) states can substitute for (+4) zirconium.

As a result of these effects, uranium and thorium in igneous rocks appear to be generally localized in those minerals that make up only a small fraction of the weight of the entire rock. In a granite from Essonville, Ontario, for example, that contains 2.74 ppm of uranium, more than 90 percent of the element is concentrated in parts of the rock which make up less than 1 percent of the total weight of the rock, with zircon and sphene retaining the major proportions. The table below shows the concentrations of uranium and thorium in the minerals of the granite at Essonville.¹ The distribution of uranium and thorium in the granite at Essonville is probably typical of many granitic bodies throughout the world.

TABLE 1.—*Distribution of uranium and thorium in granite from Essonville, Ontario*

Material	Abundance (wt percent)	Uranium content (ppm)	Thorium content (ppm)
Quartz	24	0.130	
Plagioclase	20	.204	
Perthite	52	.218	0.410
Magnetite	.4	2.57	
Apatite	.02	90.5	
Sphene	.4	303	5375
Zircon	.04	2650	2170
Composite rock		2.74	41.88
Acid-soluble material:			
Micrograms of element per gram of rock		.90	17.55
Percentage of total		29	42

Substantial amounts of uranium and thorium in the granite at Essonville are chemically so bound that significant extractions can be obtained by leaching the pulverized rock with dilute acid. Experiments with the granite showed, for example, that 29 percent of the

uranium, 42 percent of the thorium, and approximately 40 percent of the nonradiogenic lead could be readily removed by leaching the pulverized rock for a short time with cold 6M HCl.

This strongly indicates that other minor elements might be similarly localized. If this is true, it might be possible to isolate a variety of products from igneous rock without digesting the rock as a whole.

Igneous rocks ranging from tonalites to true granites and of diverse ages and geographic origins respond rather uniformly to simple acid leaching. The soluble fractions from aliquots of these rocks crushed to pass 30-mesh screens and leached with 1M HNO₃ at room temperature for 50 minutes are usually only 0.1–0.6 percent of the original weights. Ca, Fe, Al, Si, P and K are the major constituents, with Na, Mg, Ti, Mn, and other elements in the minority. The gross compositions of leaches from several granites, granodiorites, and aplites are listed in table 2. They are conspicuously different from the compositions of the rocks themselves.

Uranium, thorium, and rare-earth metals in the dissolved fractions are concentrated 20–100 times more than in the original rocks. These fractions may contain as much as 40 percent of the total weight of these elements in the rocks. Weights of extracted trace elements, determined spectrographically, are given for several diverse granites in table 3.

The rate at which the radioactive material is leached with cold acid from the granites is initially quite high and then drops off sharply. Curves showing rate of solution of radioactive materials from several granites are shown in figure 12. Increased rates are induced by higher temperature, but acid consumption from the solution of nonradioactive materials also increases markedly.

The distribution of the acid-soluble radioactive materials in granites has been examined by means of alpha-track autoradiographs of rock thin sections and through extensive separations, analyses, and studies of rates of solubility on individual minerals or selected mineral assemblages.

The alpha-track studies show that the major portion of the alpha-particle activity in most granites originates in microscopic accessory minerals. A smaller fraction of the activity occurs in the major minerals; much of this appears from the spatial relation to originate in microscopic to submicroscopic inclusions and imperfections in the coarser granitic minerals. A third type of site for the alpha tracks is along grain boundaries and fractures where from less than 10 percent to rarely more than 25 percent of the tracks may be found. This interstitial alpha activity emanates from both microscopic discrete minerals—identified with difficulty,

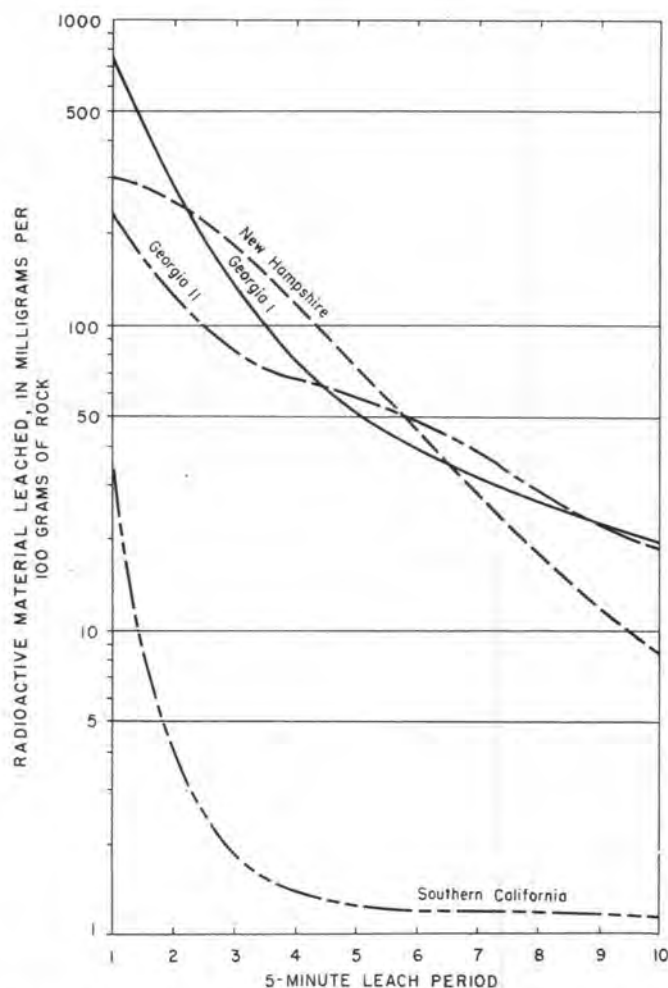
¹ Tilton, G. R.; Patterson, Claire; Brown, Harrison; and others, 1954, The isotopic composition and distribution of lead, uranium, and thorium in a Precambrian granite: U. S. Atomic Energy Comm. AECU-2840, 52 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service, Oak Ridge, Tenn.

TABLE 2.—Gross chemical composition of leaches from several types of rocks (treated with 1M HNO₃ at room temperature)

Source of sample	Total solids (mg/100g)	Constituents (wt percent) ¹								
		SiO ₂	Al ₂ O ₃ ¹	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂
Southern California.....	470	10	15	27	0.5	22	1.3	14	8.3	1.1
Georgia I.....	540	4	16	15	-----	41	.9	5.6	17	.2
Georgia II.....	310	6.8	17	15	-----	35	1.7	4.9	19	.5
Montana.....	110	7.4	19	45	1.9	14	3.2	6.9	2.6	-----
Ontario.....	150	3.4	20	47	1.2	12	3.1	8.4	5.3	-----

¹ Includes rare earths.TABLE 3.—Composition of leaches from several pulverized granites (treated with 1M HNO₃ at room temperature)

Source of sample	Total solids (mg/100g)	Radioactive material dissolved (percent)	Trace elements extracted (mg)					
			U	Th	Ce	La	Nd	Y
New Hampshire.....	420	25	0.76	4.8	4.4	2.9	2.0	0.12
Colorado.....	270	15	.38	1.1	1.6	1.1	.73	1.0
Georgia I.....	540	38	.73	3.0	9.2	5.4	4.3	.49
Georgia II.....	310	21	.50	.72	3.4	2.3	1.7	.37

FIGURE 12.—Rate of solution of radioactive materials from several granites leached with 1M HNO₃ at room temperature.

if at all—and submicroscopic particles. These particles indicate the former existence of a period of mobility for the uranium and thorium in a granite. Such periods may develop in the very late stages of rock crystallization, during a subsequent hydrothermal or metamorphic episode, or during the weathering of the rock. The distribution of alpha tracks in thin section autoradiographs of three granites is given in table 4.

TABLE 4.—Distribution of alpha tracks in thin-section autoradiographs of several granitic rocks

Source of sample	Total number of tracks	Distribution (percent)		
		Major minerals	Accessory minerals	Fractures and grain boundaries
Georgia I.....	3,255	8	83	9
Georgia II.....	2,706	14	69	17
Montana.....	1,034	26	35	39

The solubility-rate studies of various accessory minerals indicate that a few contribute significantly to the cold dilute-acid leaches. Apatite, allanite (particularly if metamict and altered), thorite, bastnaesite, and a few other species are the principal sources of radioactivity. High degrees of metamictization favor increased solubility. The apatite is responsible for much of the CaO and all of the P₂O₅ in solution, and in rocks where other soluble accessories are absent it is the principal source of radioactivity and rare earths in leaches. Allanite and highly metamict and altered aggregates which were probably originally allanite, appear to be the most important sources of radioactivity

in many of the granites examined. The composition of allanite includes most of the major constituents recognized in the leach extractions, even from rocks where the mineral itself has not been identified microscopically. This compositional factor plus allanite's common association with epidote as a deuteric and hydrothermal mineral, and the limited optical data obtained from some of the coarsest interstitial material, suggests that allanite may be an important constituent in the interstitial material in many granites.

PROCESSING

The properties of leachable material, as they have thus far been determined, suggest a number of possibilities for the isolation of uranium and thorium, with byproducts, from igneous rocks. The basic steps would be as follows:

1. Quarry the rock, crush and pulverize to grain size.
2. Leach with dilute acid and wash.
3. Neutralize solution and precipitate trace elements. This precipitate will be composed primarily of Al_2O_3 , Fe_2O_3 , and R_2O_3 and will carry down with it the uranium, thorium, rare earths, and the majority of potentially useful trace elements.
4. Allow precipitate to settle, remove supernatant solution, and dissolve precipitate in dilute acid. This solution is now sufficiently concentrated to permit direct extraction of uranium, thorium, and other useful trace elements by a sequence of straightforward chemical steps.

If it is assumed that material is being processed which possesses approximately 0.4 percent leachable matter, corresponding to 4 kilograms per metric ton of rock, acid consumption would amount to 40 moles of hydrogen ions per ton of rock processed. Retention of liquid in a pulverized rock amounts to approximately 0.3 milliliter per gram of rock or 300 liters per metric ton. Because rates of solution of leachable material drop to low levels below acid concentrations of about 0.1M, the concentration of the acid should be adjusted so that the hydrogen-ion concentration is 0.1M after leaching. If 1 ton of pulverized rock were to be barely covered with 300 liters of 0.23M acid, the hydrogen-ion concentration would drop to 0.1M following dissolution of all leachable matter.

Utilizing a cycling system involving an initial leach and five washings and using the washings to leach and wash subsequent batches, an overall yield of leachable material of about 85 percent could be obtained under steady-state operating conditions. The product-bearing solution would contain about 3.4 kilograms of dissolved solids (calculated as oxides) per 300 liters, or 11 grams per liter. The solution under steady-state operating conditions would have an acid concentration of about 0.063M. Somewhat over 60 moles of hydrogen ions and 600 liters of water would be consumed per ton of rock processed.

ENERGETICS AND COSTS

Average granite contains approximately 4 ppm uranium and 12 ppm thorium. If all the uranium and thorium could be extracted from 1 ton of rock, then converted to fissionable material and fissioned in a nuclear reactor, the energy release would be equal to that obtained from burning about 50 tons of coal. It has been seen that on the average about 25 percent of the uranium and thorium in a granite is leachable, and that an actual process yields about 85 percent of the leachable material. Thus, if nuclear breeding and the isolation only of the leachable material are assumed, 1 ton of granite is equivalent in releasable energy content to about 10 tons of coal.

The energy requirements for processing 1 ton of granite must now be determined. Clearly, if this were less than the equivalent of 10 tons of coal, average rock could be processed with a net energy profit.

The energy requirements for quarrying rock, reducing from haulage size to 10-inch pieces, crushing to 0.25-inch size, and pulverizing to less than 50 mesh has been surveyed by the authors. It appears that these steps would require between 7 and 9 kwhr per ton of rock. Acids and other chemicals would cost between 10 and 25 kwhr per ton, depending upon the acid used (the higher value is computed for nitric acid). Additional direct-energy costs involving disposal of wastes, water pumping, movement of other materials through the process, and maintenance and shop facilities would be about 1 kwhr per ton. To these figures must be added such hidden energy costs as original capital investment, replacement of equipment, and transportation to and from the plant. These are difficult to estimate, particularly if all hidden energy costs are taken into consideration. However, calculations by the author indicate that all hidden costs combined might be expected to be between 0.7 and 2.3 kwhr per ton.

These values added together suggest that total energy requirements, both direct and hidden, would probably lie in the range of 19 to 37 kwhr per ton of rock processed. If it is assumed that 1 kwhr is equivalent to 1.3 pounds of coal burned at 20 percent efficiency, the energy costs would lie in the range of 25 to 48 pounds of coal per ton of rock processed. This is clearly very much smaller than the energy equivalent of 20,000 pounds of coal which could be extracted from a ton of average rock.

Thus, when the problem is viewed solely from the point of view of energetics it is clear that most of the granitic rocks of the earth's crust are at mankind's disposal and can be processed for a net energy profit. This means that the reserves of uranium and thorium available to man can be considered for all practical purposes as infinite.

Costs per ton of rock processed probably lie in the range of \$1.00 to \$2.25 per ton, depending upon the way in which the uranium and thorium are held in the rock and the type of acid used in the processing. This means that if only average granites were processed and no part of the operating cost could be assigned to by-products, uranium could be produced at a cost of \$550-\$1,200 per pound. If thorium is considered to possess one third the value of uranium, the corresponding approximate cost ranges would be \$270-\$600 per pound for uranium and \$90-\$200 per pound for thorium. Values of byproducts would reduce these prices by amounts which are yet to be determined. If byproducts valued at about \$1.00 per ton of rock could be obtained, as seems possible, the maximum cost of uranium from average granite would be about \$340 per pound.

It is clear that average granite cannot be processed economically at the present time, but there are large bodies of igneous rocks which possess higher-than-average leachable uranium and thorium contents.

CONCLUSIONS

A substantial fraction of the uranium, thorium, and certain other elements present in igneous rocks can be readily removed by leaching with dilute acid.

More energy can be obtained from average granite in the form of uranium and thorium than is required for processing the rock.

Although the cost of processing average granite is prohibitively high at the present time, a number of igneous bodies possess higher-than-average concentrations of leachable uranium and thorium. Some of these bodies might well be processed competitively in the near future.

Uranium and thorium in the igneous rocks of the earth's crust is sufficient to power a highly industrialized world economy for a very long period of time.

When the situation is examined solely from the point view of availability, no nation which needs uranium and thorium in quantity need be deprived of supplies of these elements.

Contributions to the Geology
of Uranium and Thorium by the
United States Geological Survey
and Atomic Energy Commission
for the United Nations International
Conference on Peaceful Uses of
Atomic Energy, Geneva, Switzerland
1955

Compiled by LINCOLN R. PAGE, HOBART E. STOCKING, *and*
HARRIET B. SMITH

GEOLOGICAL SURVEY PROFESSIONAL PAPER 300

*Prepared as a cooperative effort of the United States
Geological Survey and the United States Atomic
Energy Commission and published with the per-
mission of the Commission*



UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1956